

# Tungsten: A Preliminary Environmental Risk Assessment

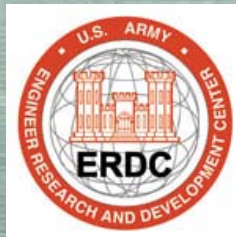
David R. Johnson

Environmental Laboratory

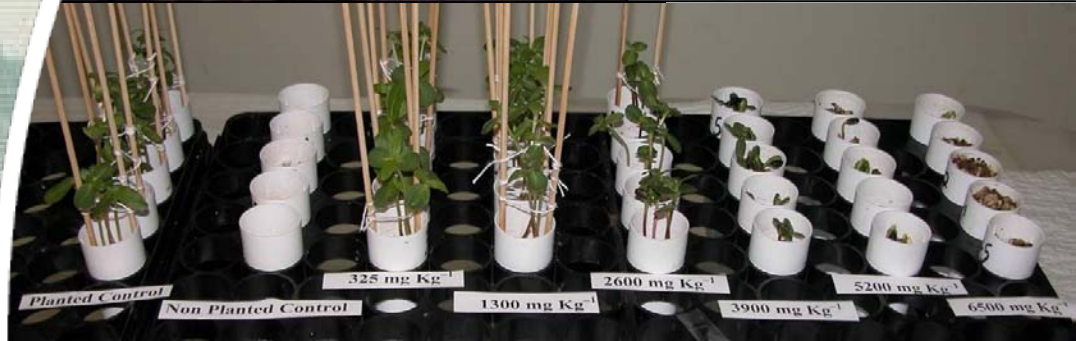
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Development Center

Vicksburg, MS

June 17, 2010



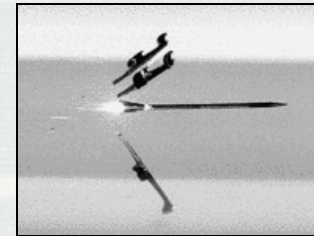
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# ***Tungsten: Characteristics & Military Applications***

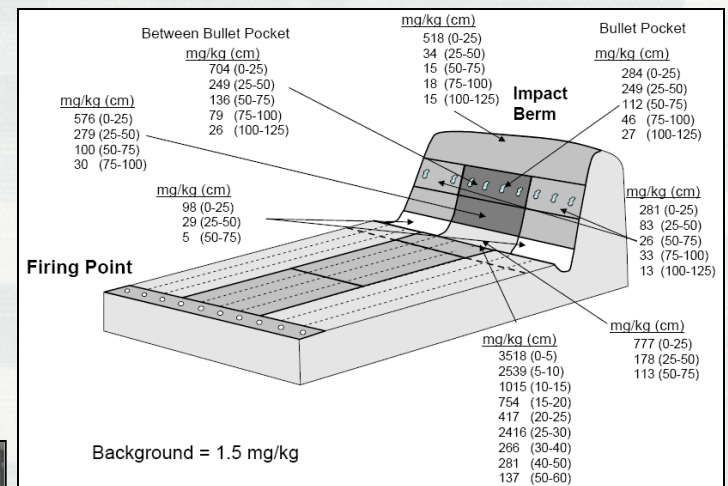
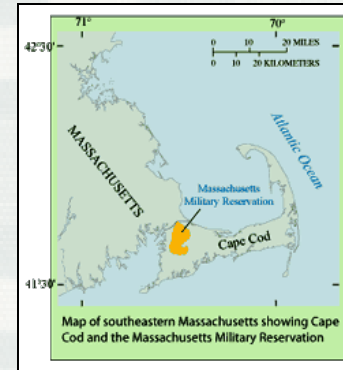
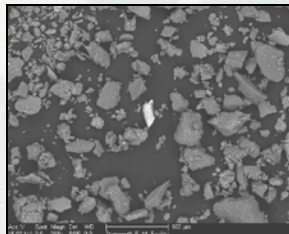
- Only small percentage of earth metals  
~1 mg/kg (ppm)
- Found in ores in multiple oxidative states ( $W^{-4}$ ,  $W^{-2}$ ,  $W^{-1}$ ,  $W^{+3}$ ,  $W^{+5}$ ,  $W^{+6}$ )
- 2nd most dense metal
- Highest melting point
- Highest tensile strength
- Military uses:
  - Small arms munitions
  - Penetration ammunition
  - Protective armor plates



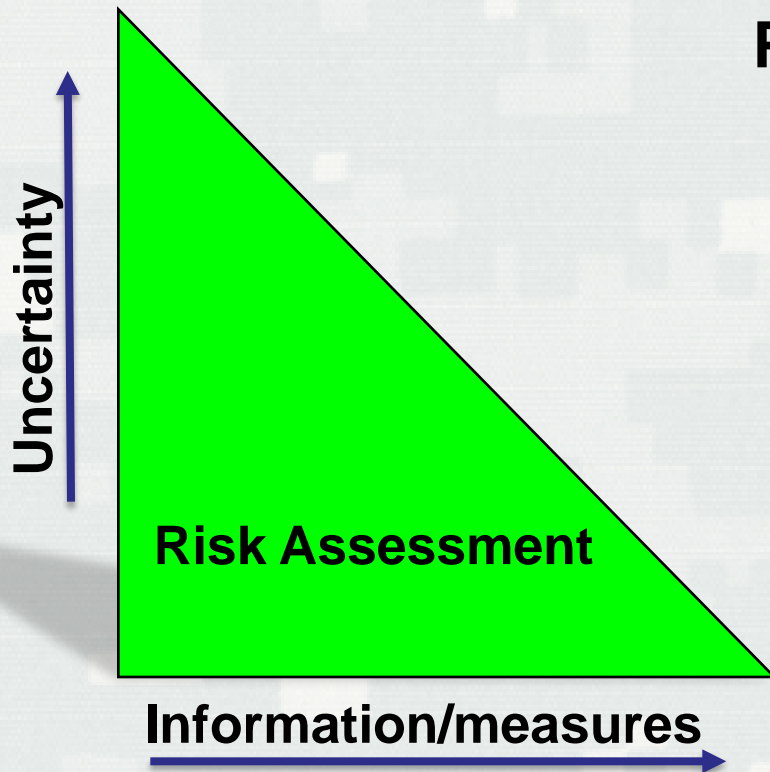


# Problems with Tungsten: Environmental Mobility

- “Green bullets” used for training in late 1990s & early 2000s as alternative to lead bullets
- Tungsten powder (~1 mm) in nylon matrix
- “Environmentally benign”
- Tungsten detected in groundwater
- Concern of ingestion from drinking water
- Inconclusive health effects
- Unknown environmental effects



# ***Reducing Uncertainty in Risk Assessment***



**Problem:** Need to increase knowledge of the potential impacts of military unique compounds and industrial compounds on aquatic and terrestrial wildlife species

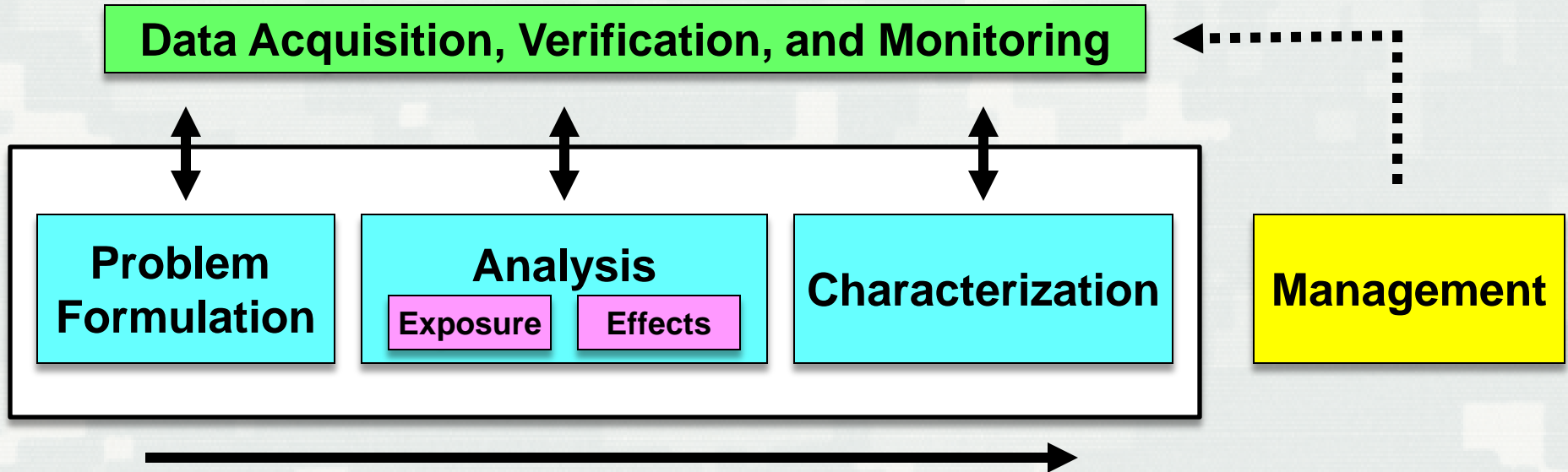
***UNCERTAINTY = \$ COST \$***

***SOLUTION:***

***MORE KNOWLEDGE = IMPROVED ASSESSMENTS =  
MORE TRAINING = BETTER SOLDIERS***



# ***Ecological Risk Assessment Framework***



- Process that evaluates the likelihood that adverse effects may occur or are occurring as a result of exposure to one or more stressors (USEPA, 1997)
- Risk management is an approach to consider the outcome and uncertainty of an assessment and mitigate risk through a range of alternatives.



# ***Relevance: Are Environmental Tungsten Levels Likely to Cause Biochemical Effects?***

**Dietary uptake:**     ~0.01 mg  
                              0.2-16 mg/kg (vegetables)

**Drinking water:**    generally not measured  
                              0-217 µg/L (Fallon, NV)  
                              groundwater > surface water

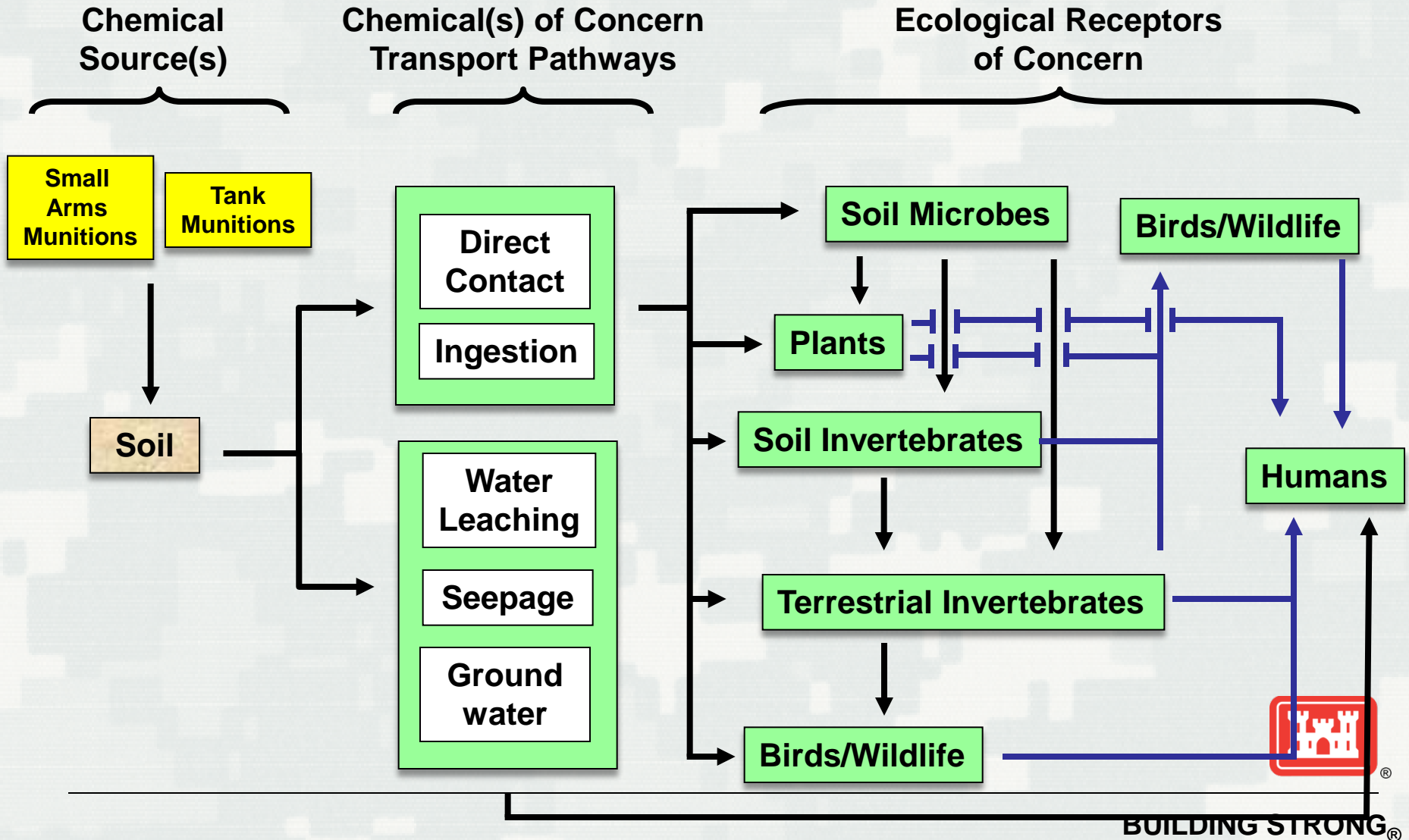
**Soil:**                    1-1.3 mg/kg (earth's crust)  
                              1-22 mg/kg (agriculture fields)  
                              0-5,500 mg/kg (tungsten mines, military ranges) ★

**Air:**                    < 10 ng/m<sup>3</sup> (ambient)  
                              5 mg/m<sup>3</sup> (industry, OSHA)





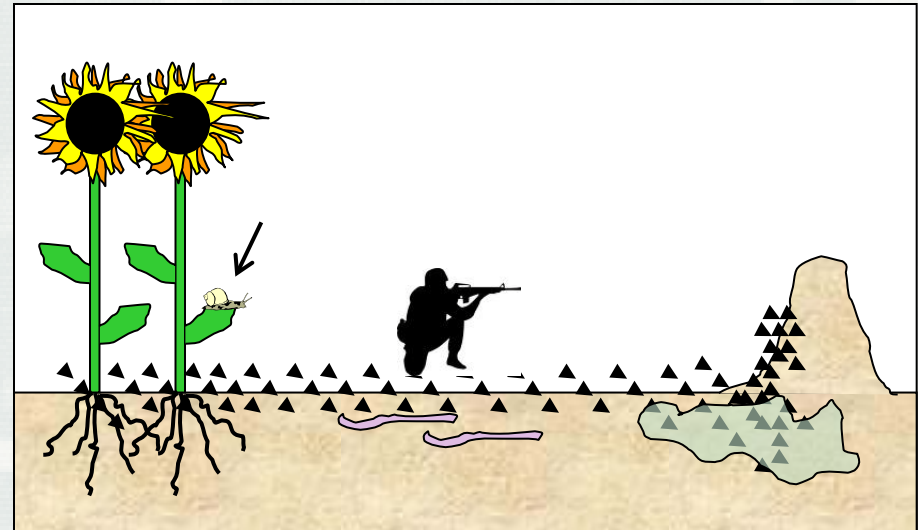
# ***Tungsten: Ecological Risk Assessment Conceptual Model***





# ***Tungsten Research To Assess Exposure and Effects on Flora & Fauna***

- **Geochemistry**
- **Soil microbial communities**
- **Plants**
- **Soil invertebrates**
- **Higher order animals**
- **Additional studies**

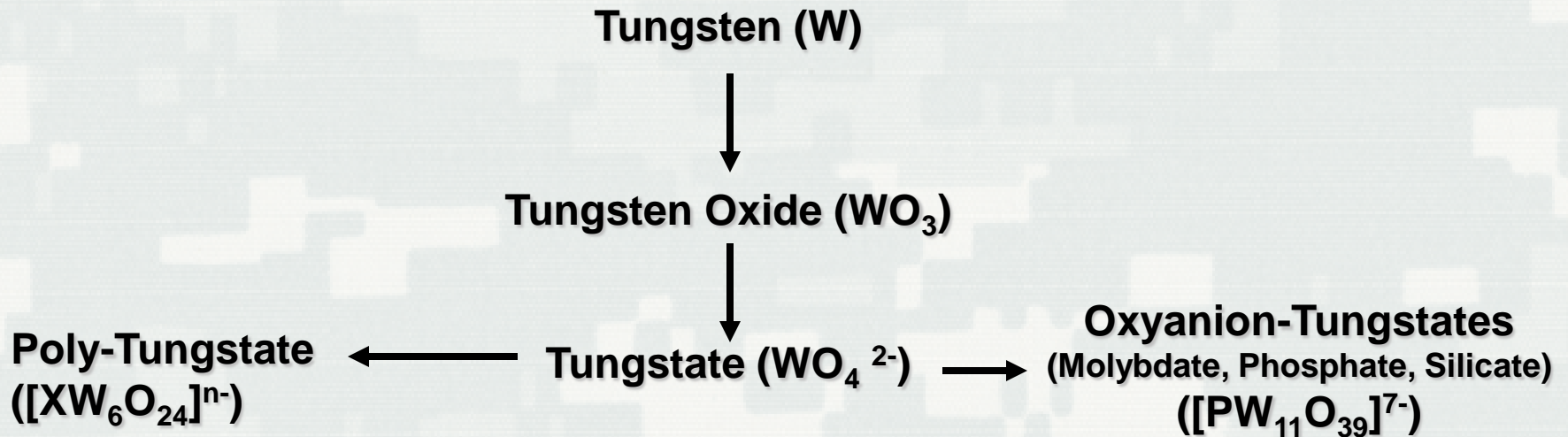


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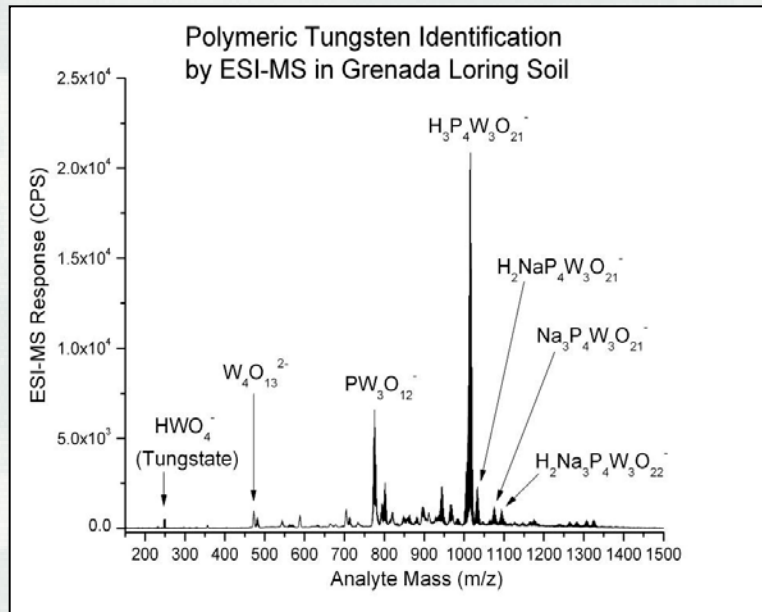
# ***Tungsten Geochemistry***

**Geochemistry of tungsten in soils will affect:**

- **Speciation**
- **Mobility/sorption in soil**
- **Microbe, plant, and invertebrate uptake**
- **Differential toxicity from parent compound and chemical species**



# Tungsten Geochemistry: Chemical Speciation in Soil



Tungsten Compounds	$K_d$ 3 Days	$K_d$ 4 Months
Tungstate	284	845
Polytungstate	92	135
Phosphotungstate	112	500
Tungstosilicic Acid	103	97

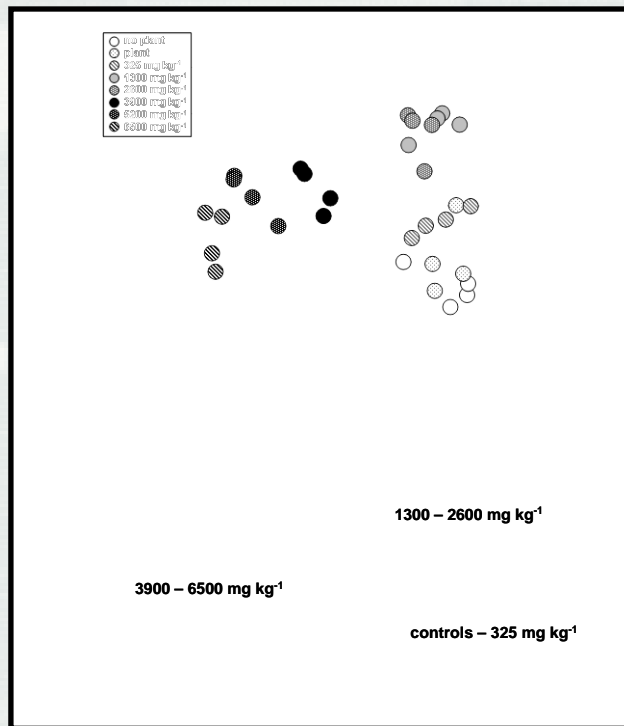
★ 1 yr aged soil  $K_d = 110$

Partition coefficients ( $K_d$ ), a measure of sorption, suggest that different species will have different mobility in soil

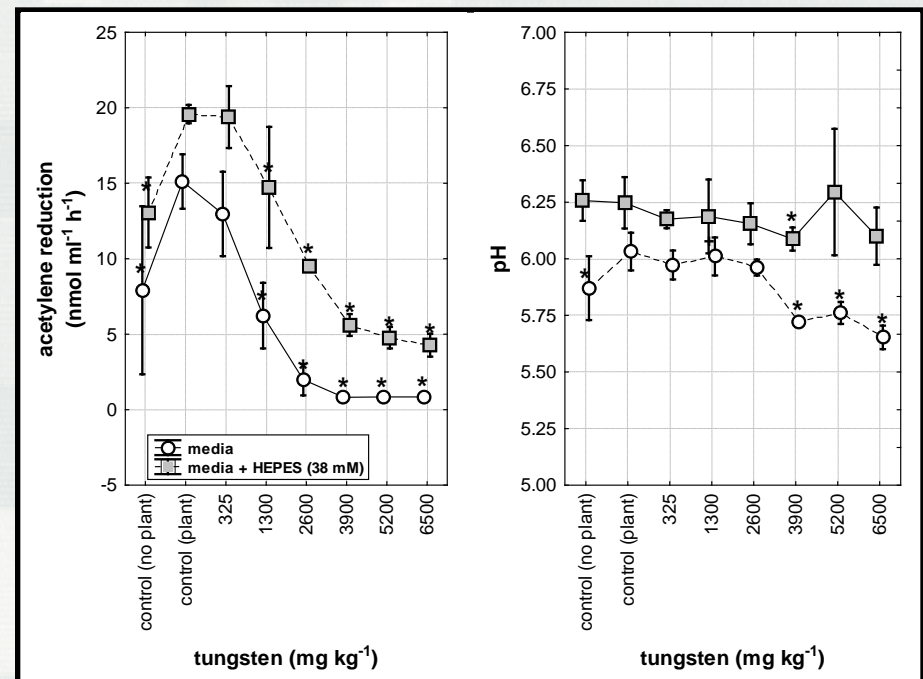


# Tungsten Effects on Soil Microbial Communities

- W caused significant shifts within the *in situ* microbial community with increasing soil W concentrations
- W significantly decreased nitrification activity in a pH-independent manner



Shift in microbial community structure w/ increasing [W]



Nitrification activity inhibited by increasing [W] at neutral pH

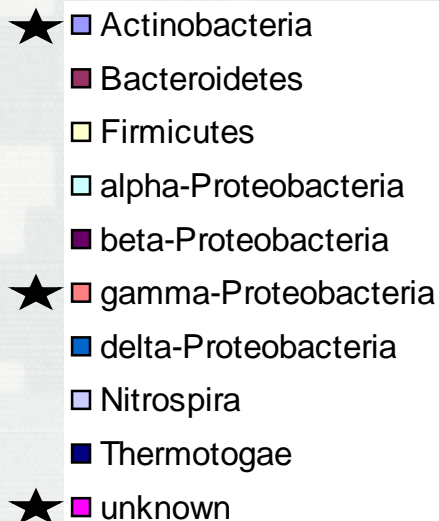
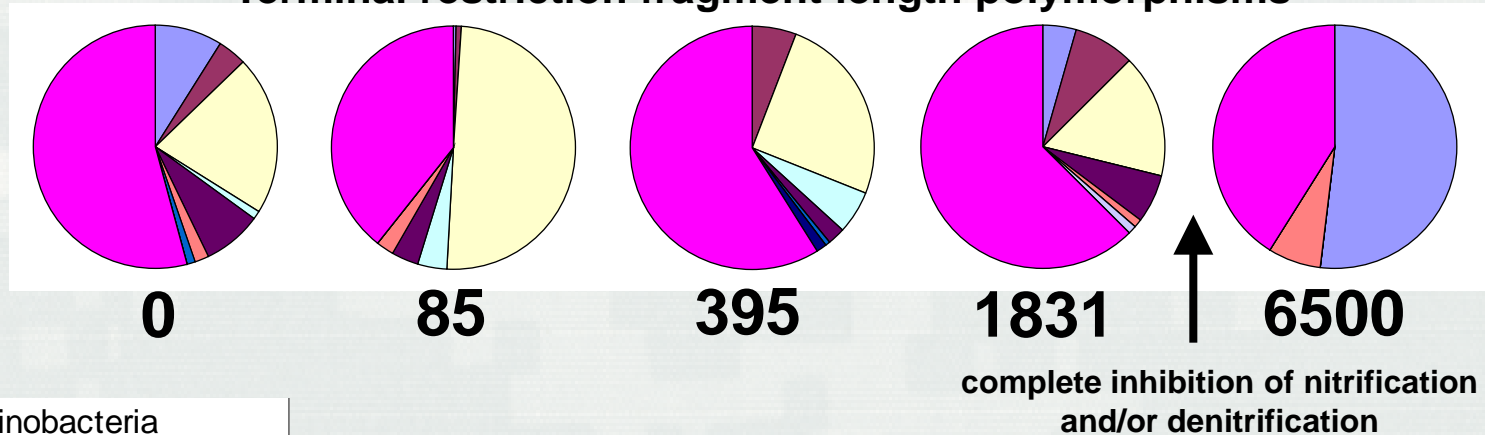




# Tungsten Effects on Soil Microbial Communities

- We then characterized the observed community shifts and identified a loss in species diversity

Terminal restriction fragment length polymorphisms



## Increasing soil [W] resulted in:

- Loss in diversity
  - Effect on Soil Quality
- Persistence of Actinobacteria & gamma-Proteobacteria
  - Actinobacteria – includes the actinomycetes
  - $\gamma$ -Proteobacteria – includes a variety of microbes



# ***Bioaccumulation of Tungsten in Plants***

## **Natural Sources**

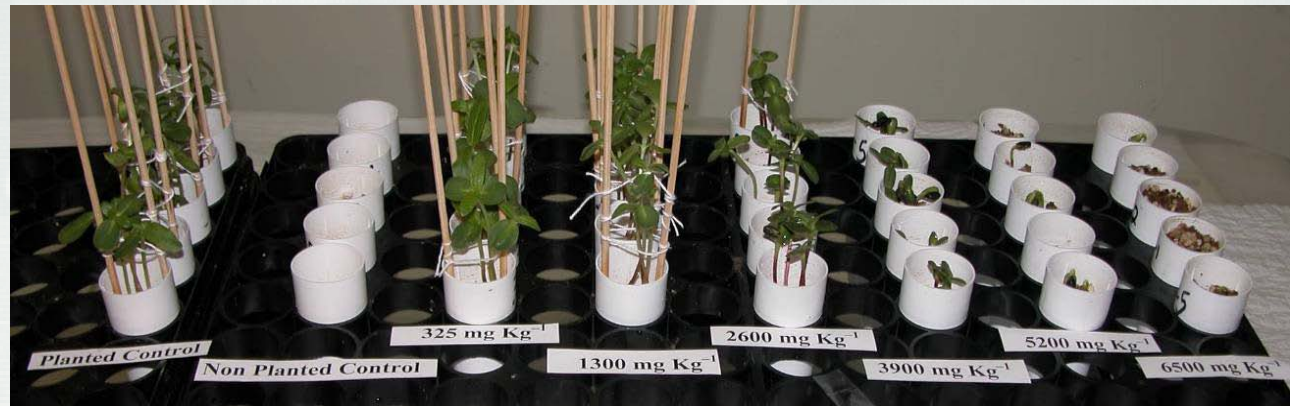
- Trees & shrubs in Rocky Mountain region, USA
- Siberian pine, willows, mosses & lichen in tungsten-rich fissures

## **Anthropogenic Sources**

- Agriculture & fertilizers (e.g., chemical, municipal biosolids, incinerator ash)
- Industry (e.g., manufacturing facility wastewater discharge)
- Abandoned mines
- Military



# Effects of Tungsten-Spiked Soil on Sunflowers



0 325 1300 2600 3900 5200 6500

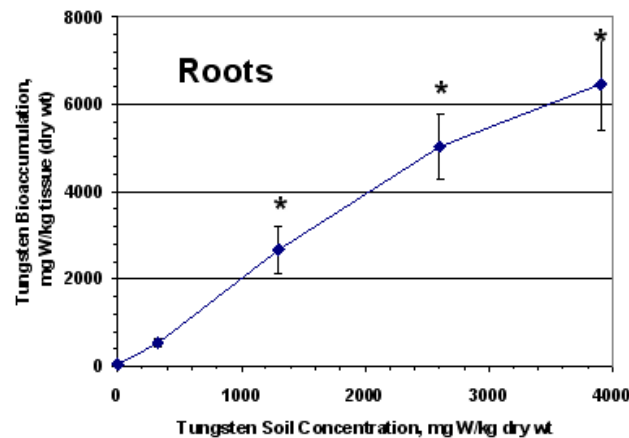
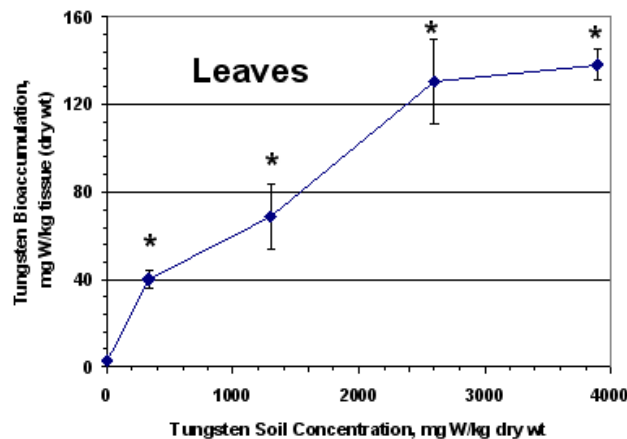
Soil Tungsten Concentration, mg/kg

Statistically  
significant  
changes at  $\geq [x]...$

↑  
Stem Wt

↑  
Leaf Wt  
Total Wt

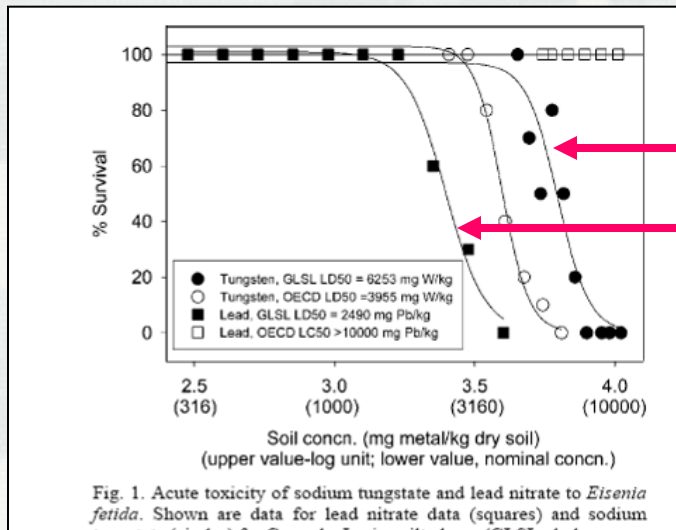
↑  
Root Wt  
Shoot Length  
Root Length



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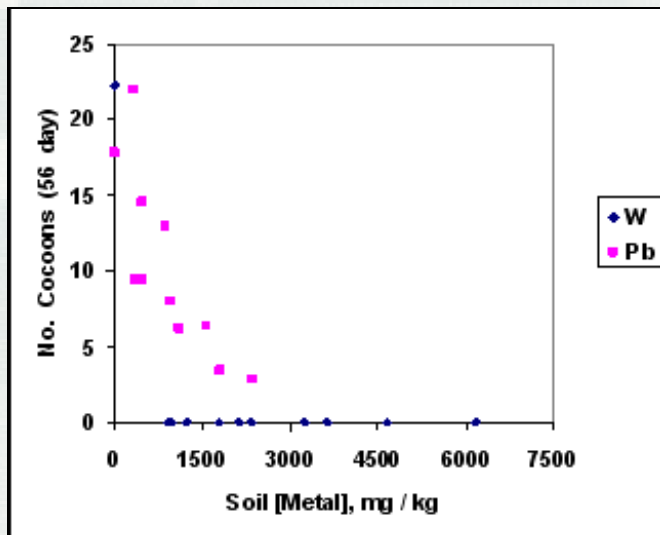
# Effects of Tungsten on Earthworms (*E. fetida*)



W (field soil) LD50 = 6253 mg/kg

Pb (field soil) LD50 = 2490 mg/kg

- W is less acutely toxic to earthworms than lead

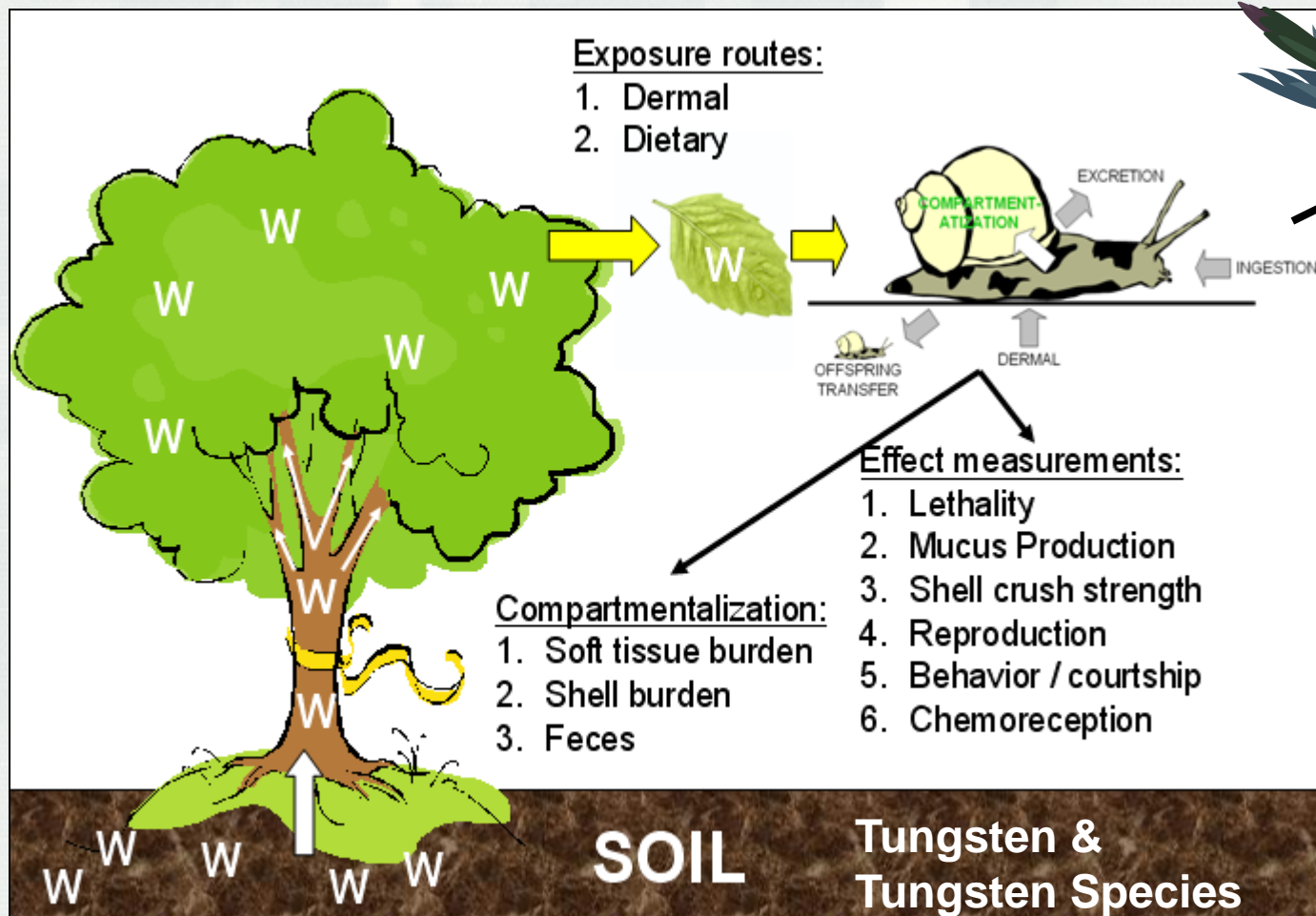


- W is a potent reproductive toxicant to earthworms after 28 day exposure

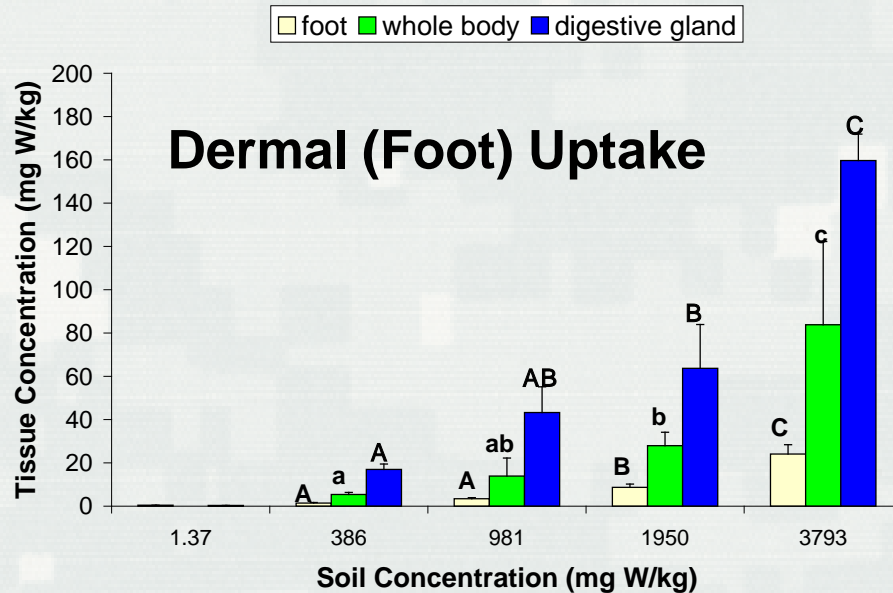




# Is Tungsten Transferred Up the Food Web?



# ***Uptake of W in Gastropods***

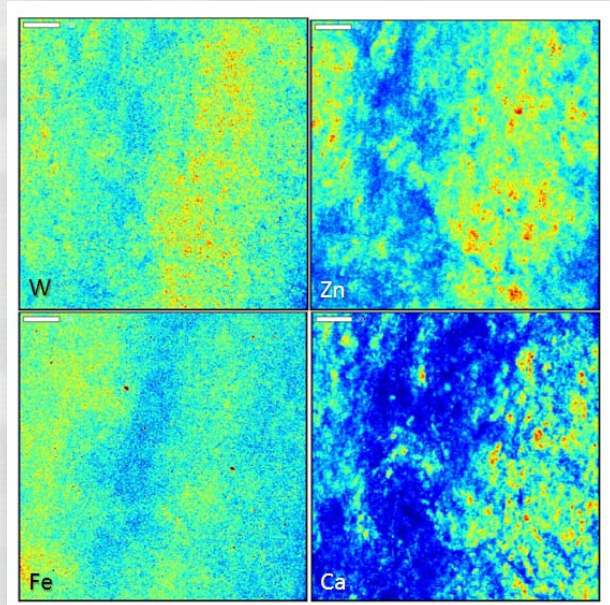


## **Steady State:**

**Body: 14 days**

**Hepatopancreas: 23 days**

**BAF: 0.09**



**Synchrotron analysis of  
Snail hepatopancreas**



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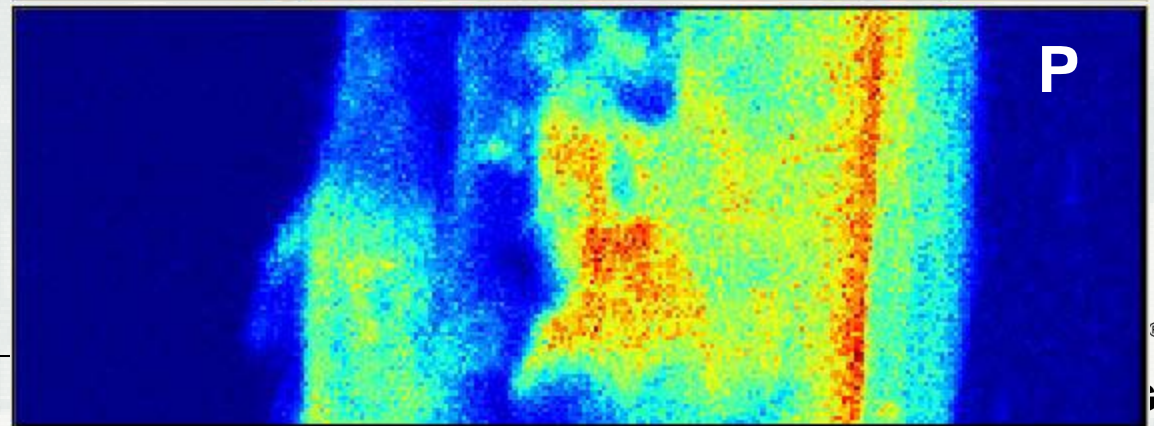
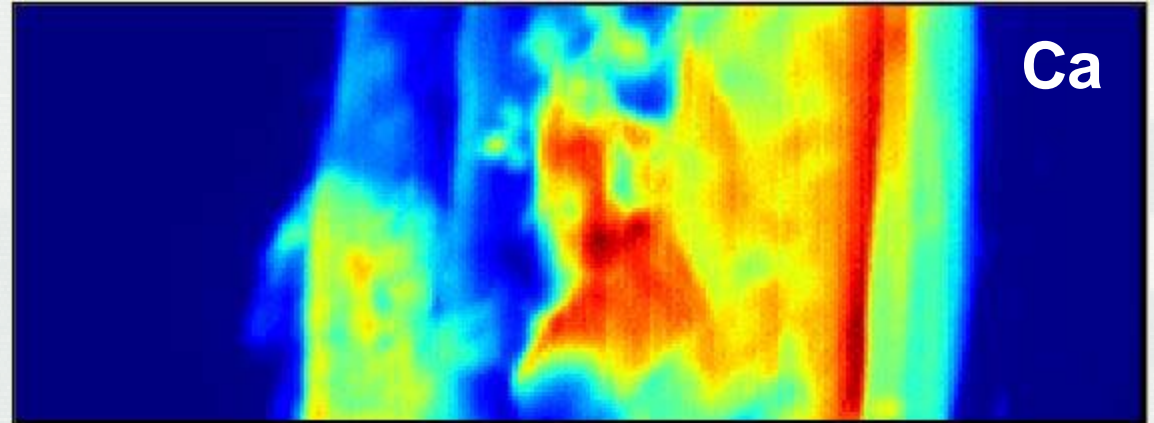
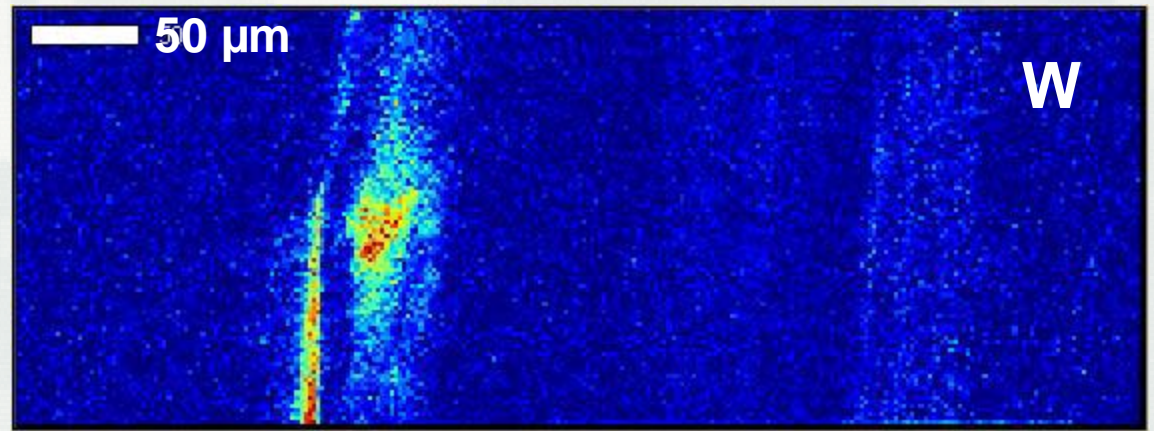
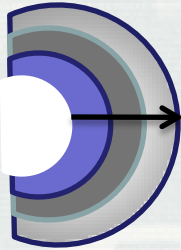


# *Dermal Uptake of W in Gastropods*

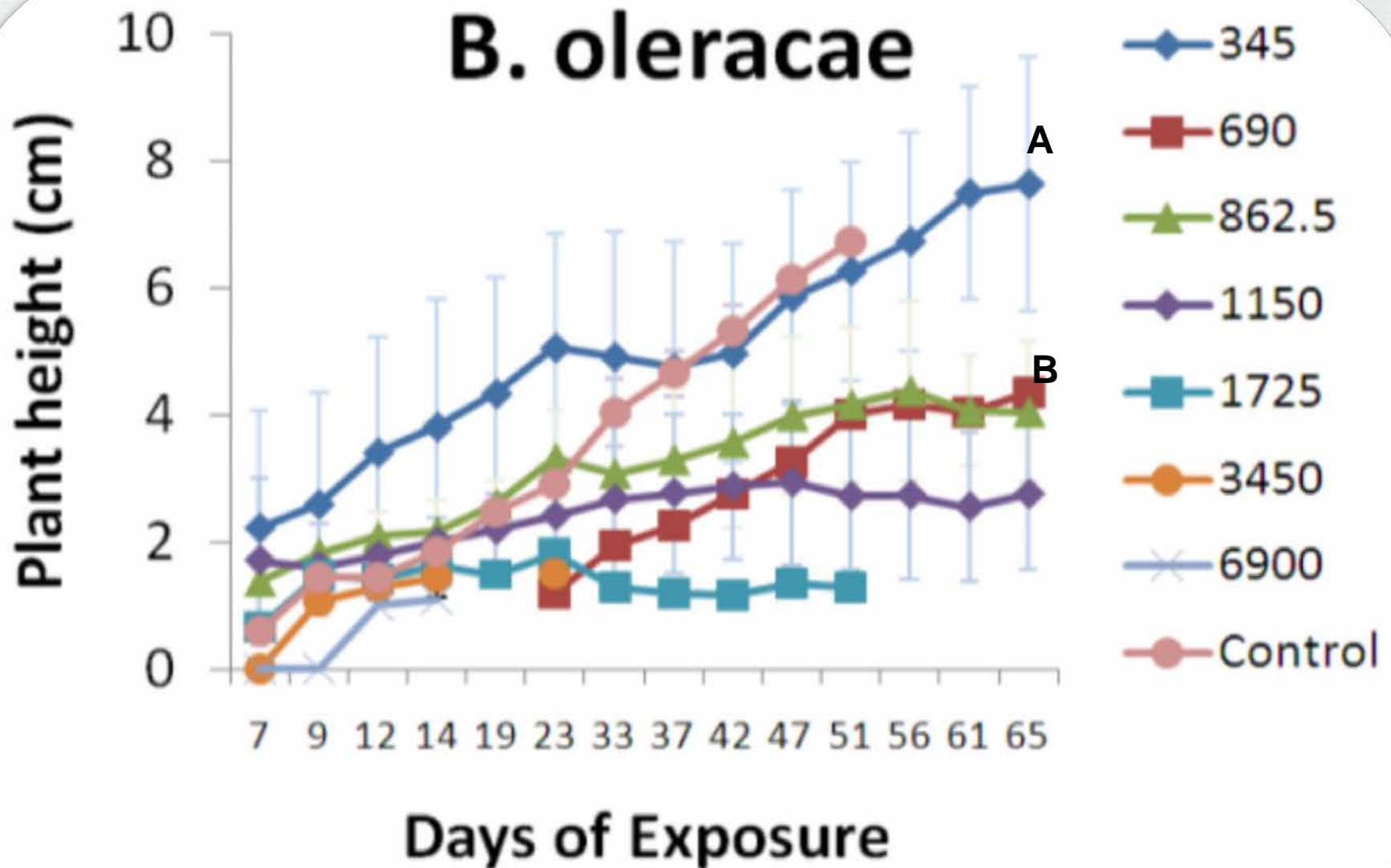
Snail Exposed to W



Shell Cross  
Section



## *Uptake of W in Gastropod Food Source*





# ***Uptake of W in Gastropod Food Source***

**Exposed to**

**Cabbage (251 mg/kg)**

**Soil ( $547 \pm 34$ ) mg/kg soil**

**Rates**

**Hepatopancreas**

**Uptake ( $k_u$ ):  $0.23 \pm 23$  g/g/d  
( $p=0.40$ )**

**Elimination ( $k_e$ ):  $0.63 \pm 0.68$  1/t  
( $p=0.43$ )**

**Steady state: 5-days, 85.9 mg/kg**

**BAF = 0.36**

**Body**

**Uptake ( $k_u$ ):  $0.05 \pm 0.03$  g/g/d  
( $p=0.15$ )**

**Elimination ( $k_e$ ):  $0.35 \pm 0.21$  1/t  
( $p=0.19$ )**

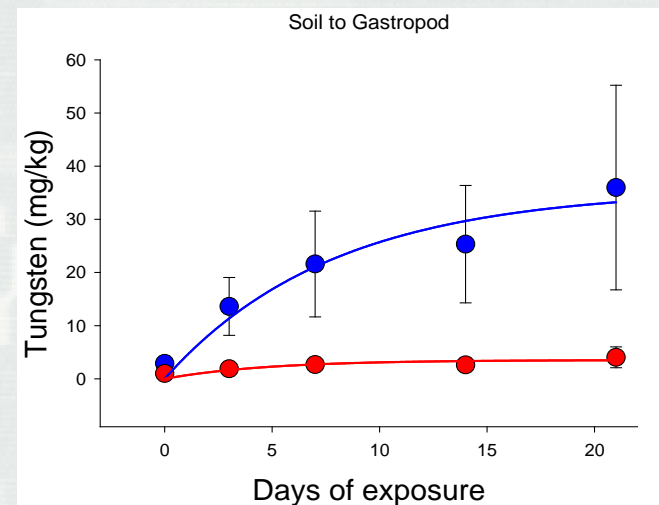
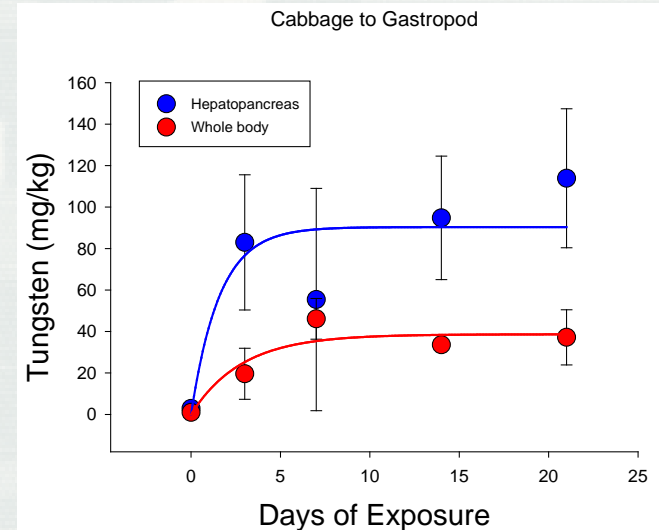
**Steady state: 9-days, 36.7 mg/kg**

**BAF = 0.15**

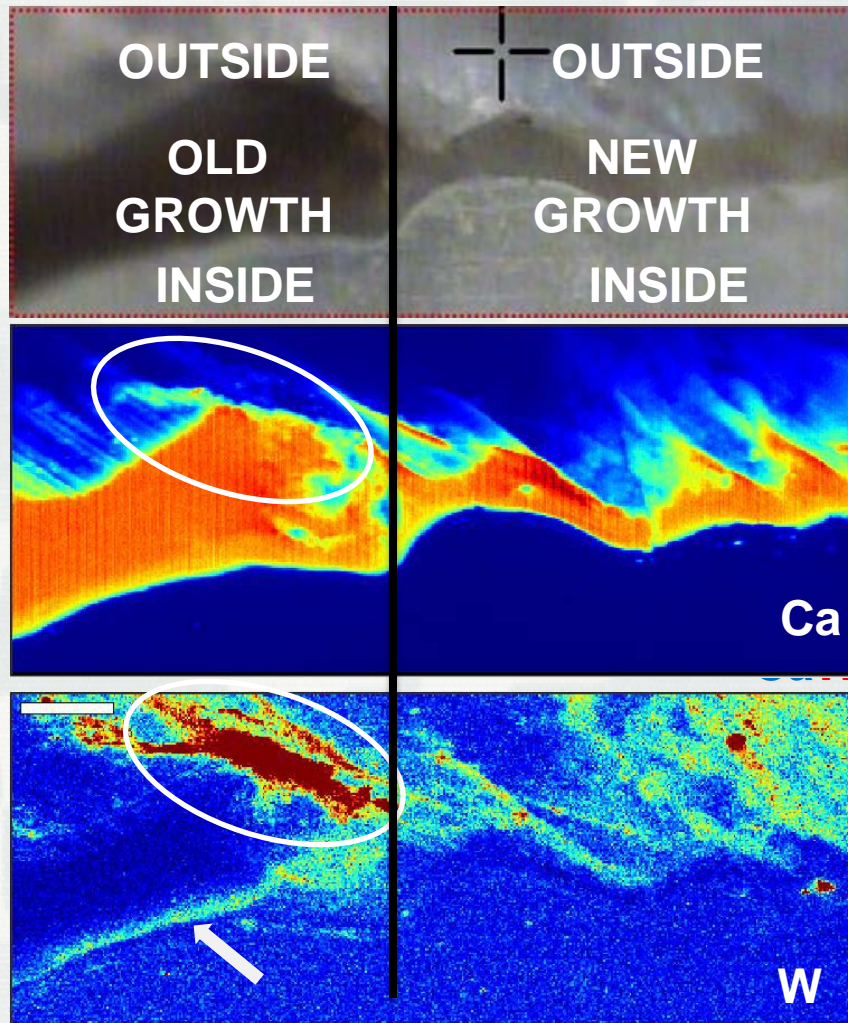
**Body/liver = 0.43**

**Only 0.09 in soil exposure**

**Assimilation efficiency greater**



# ***Uptake of W in Gastropod Food Source: effect on gastropod shell***



Cross section of shell  
Ca map clearly shows  
face

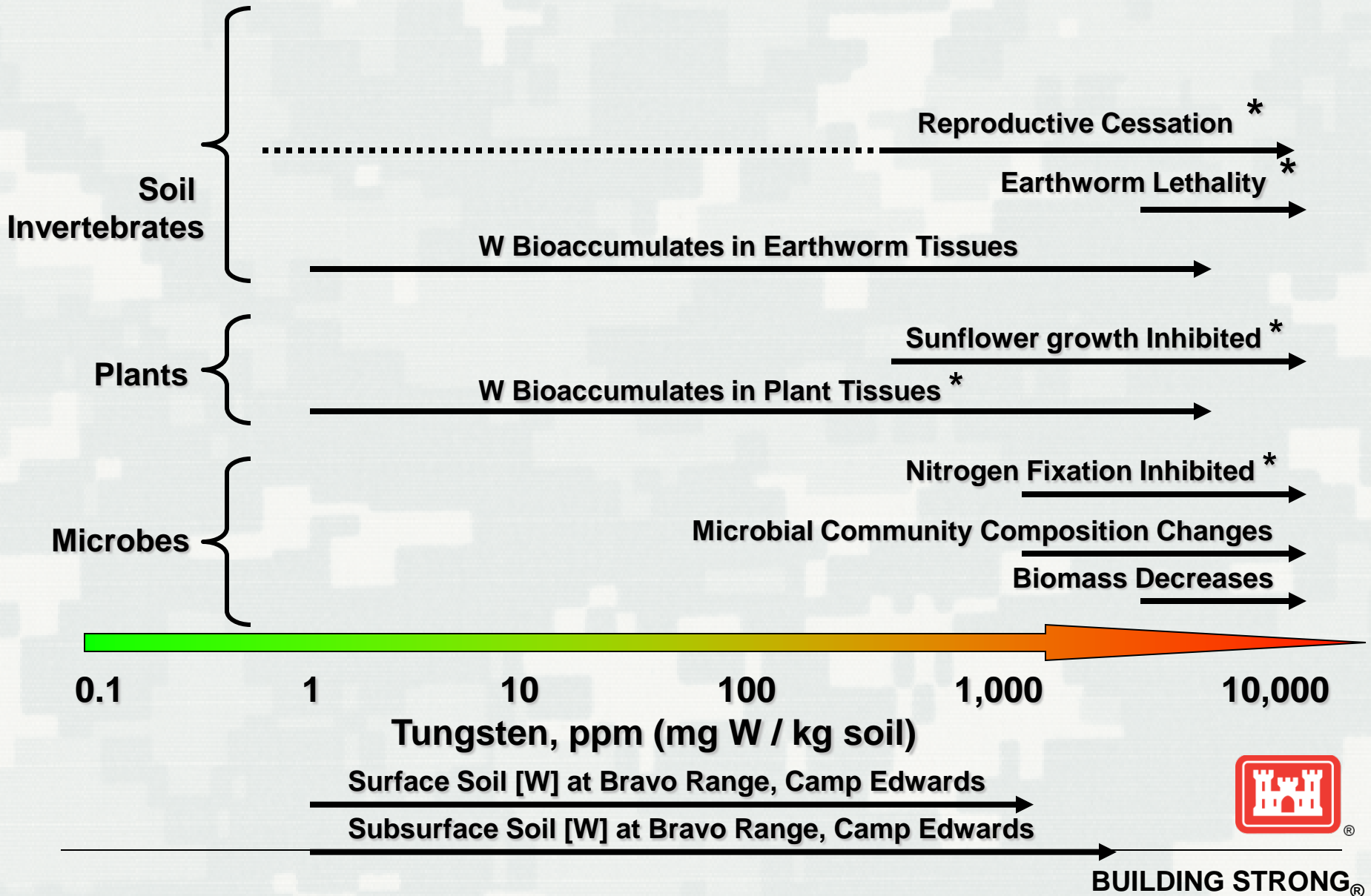
W clearly on the inside of  
the shell

Hot spot  
ICP-MS:

5.7 vs.  $< 0.1$  mg/kg

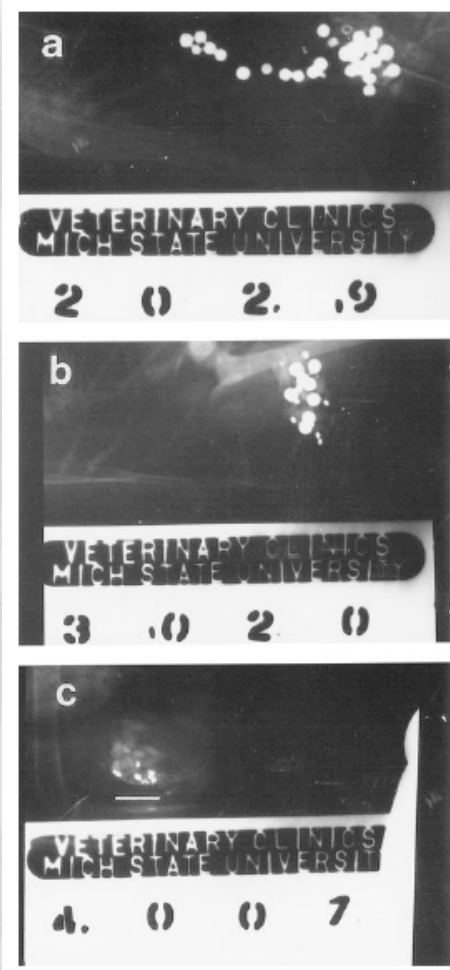


# Tungsten Ecotoxicity: Fate & Effects

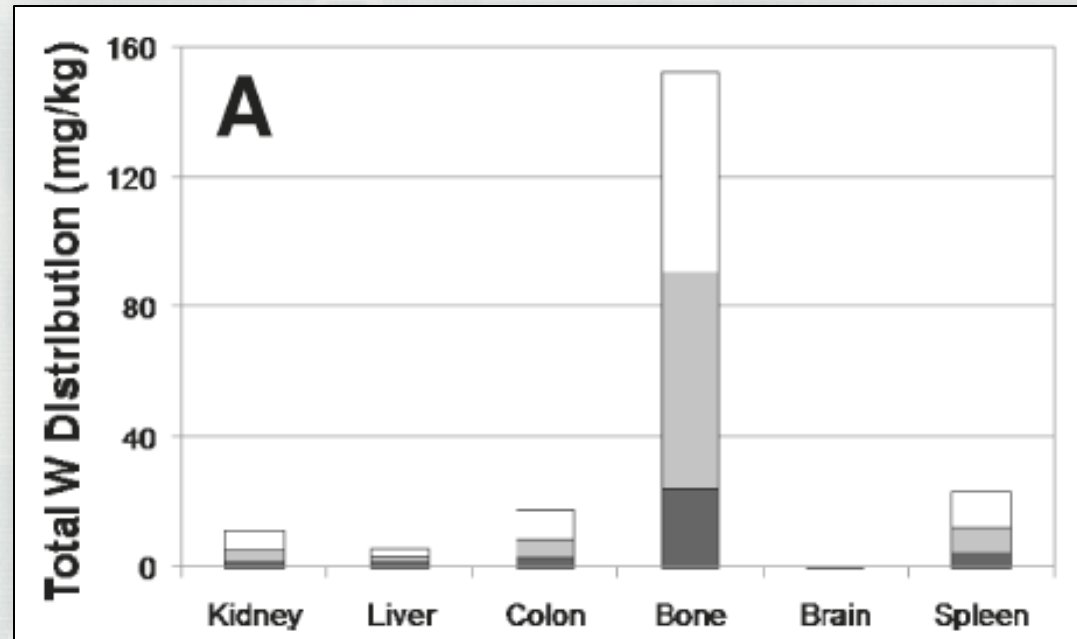




# ***Tissue Distribution of W Uptake in Higher Organisms***



Mitchell et al. 2001



Guandalini et al. 2011

Steel: 50 % erosion  
W-FE: 64% erosion  
W-polymer: 98% erosion



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# ***Is Tungsten Affecting Cellular Biochemistry and Physiological Processes in Liver Cells?***

- Moderate W concentrations in liver after acute exposure
- Direct route to liver for oral ingestion
- Liver contains high levels of Mo-containing enzymes... competition at Mo-binding sites?
- Glucose metabolism pathways affected by W
- Tungsten binds to oxyanions (i.e., phosphates) in soil... does it happen in the body too?
- If tungsten binds oxyanions, is it affecting/ interfering phosphate-dependent pathways?

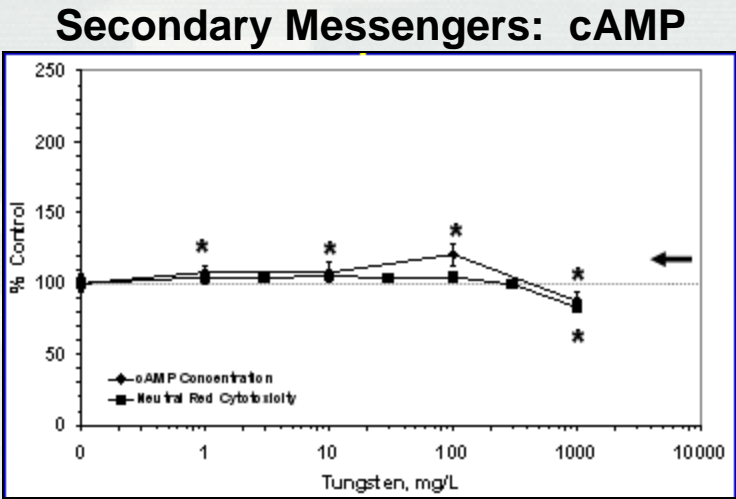
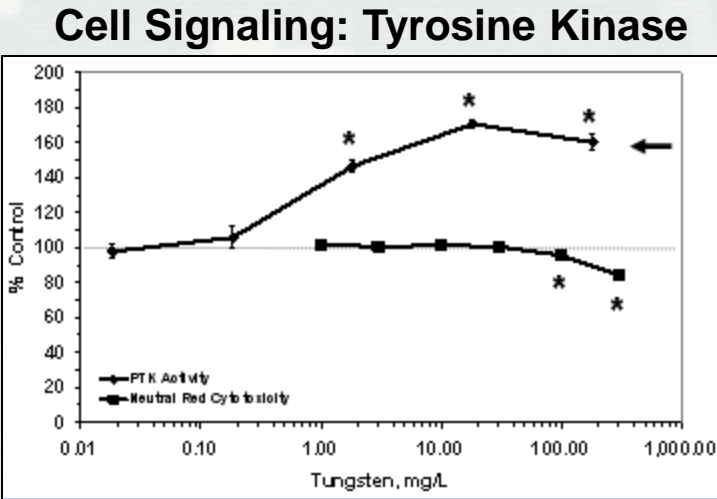
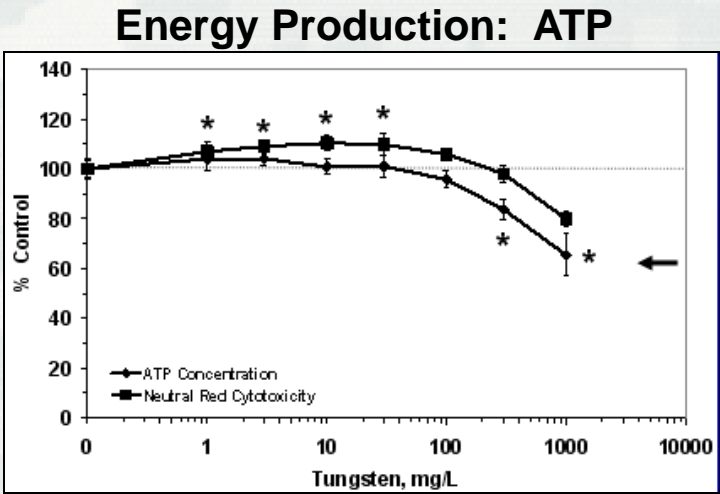


# Tungsten Bioaccumulation & Effects on Phosphate-Dependent Biochemical Pathways in the HepG2 Hepatic Cell Line

	Uptake		
	Dissolved W <sup>a</sup> (ug/L) (ppb)	Tungstate <sup>b</sup> (ug/L) (ppb)	Polytungstate <sup>b</sup> (ug/L) (ppb)
Control	< 20	<10	<10
1000 ppm W	1100	871	34

<sup>a</sup> Analyzed by ICP-MS

<sup>b</sup> Analyzed by SEC-ICP-MS



# ***Toxicogenomic Effects of Tungsten on Rat Hepatocytes***

**1,822 Up-Regulated genes**

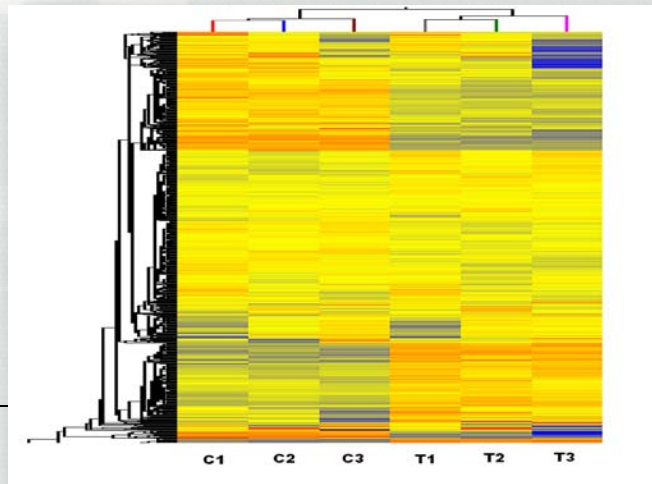
## **Major pathways affected:**

- Nucleic acid metabolism
- Macromolecule synthesis
- Caspases / apoptosis
- Cell proliferation
- Transitional metal ion binding
- Peptidase activity
- DNA & protein binding

**1,802 Down-Regulated genes**

## **Major pathways affected:**

- Lipid metabolism
- Glycoprotein metabolism
- Oxidoreductase activity
- Stress response
- Transferase activity
- Catalytic activity
- Membrane-bound organelles
- Membranes
- Regulating apoptosis
- Developmental processes
- Protein modification
- Mitochondria



# ***Conclusions***

## **Geochemistry:**

- **Aging of tungsten in soil results in heteropolymeric speciation**

## **Microbes:**

- **Tungsten significantly decreases nitrification, potentially affecting plant health**
- **Tungsten causes a decrease in microbial community diversity, resulting in poorer soil quality**

## **Plants:**

- **Tungsten significantly affects sunflower growth**
- **Tungsten (species) bioaccumulates in plant tissues**

## **Invertebrates:**

- **Earthworm reproduction blocked by tungsten**
- **Tungsten bioaccumulates in snails via foot exposure and diet**
- **Tungsten bioaccumulates in snail shell**

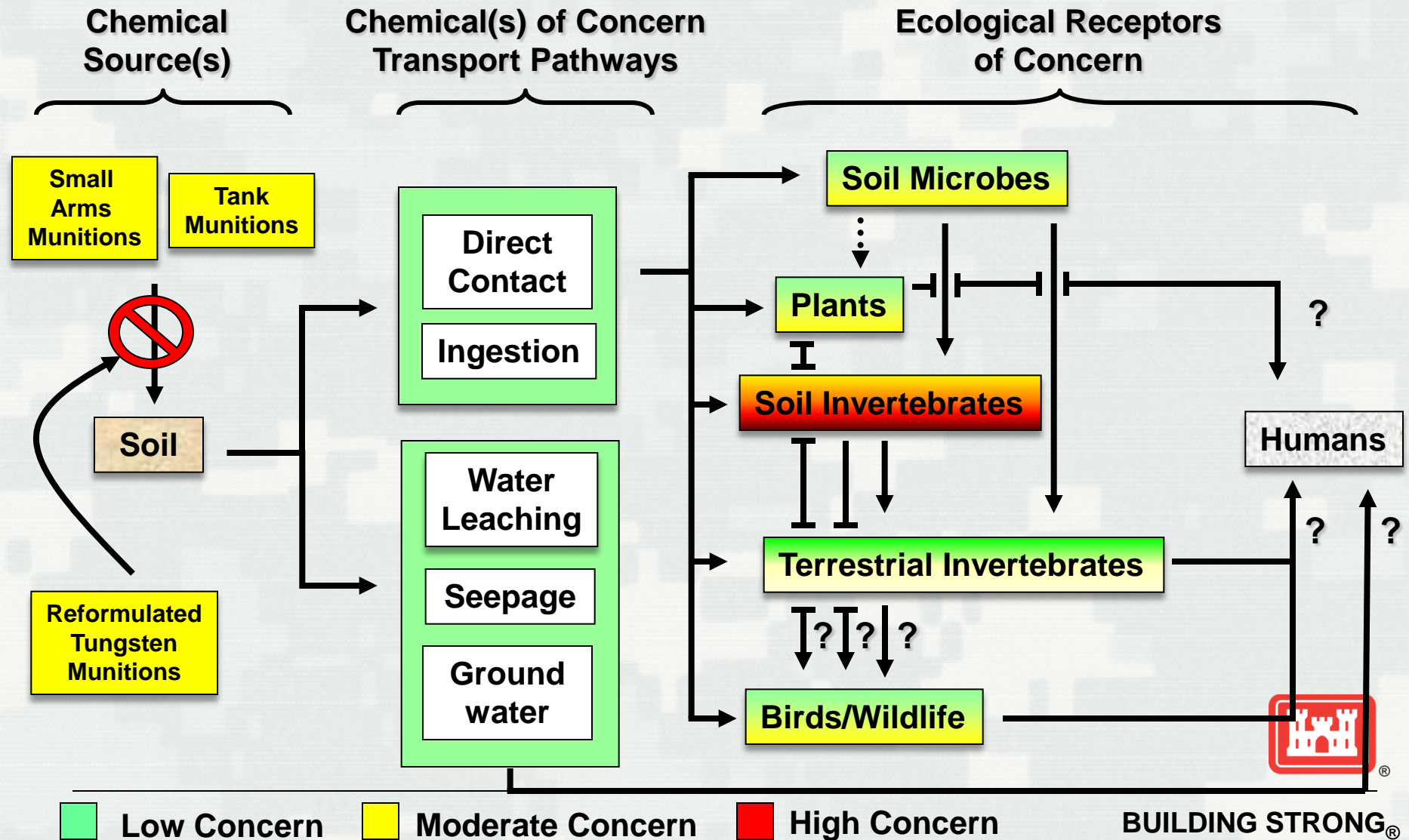
## **Higher Organisms:**

- **Tungsten (at medium to high concentrations) significantly affects phosphate-dependent cell signaling pathways and secondary messengers in a liver cell culture**





# ***Tungsten: Ecological Risk Assessment Conceptual Model***



# ***Thank You for Your Time and Attention***

- **Anthony Bednar & Will Jones (EL): Environmental Chemistry**
- **Mark Chappell & Jen Seiter (EL): Soil geochemistry**
- **Chris McGrath (EL): Geochemical modeling**
- **David Ringelberg (CRREL): Microbiology**
- **Linda Winfield (retired): Plant Biology**
- **Robert Boyd (EL): Terrestrial Ecotoxicology (plants & earthworms)**
- **Alan Kennedy & Jay Lindsay (EL): Terrestrial Ecotoxicology (gastropods)**
- **ChooYaw Ang (BTS): Cellular Biology**
- **Laura Inouye (Washington State Dept. of Ecology): Terrestrial Ecotoxicology & Cellular Biology**

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